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(54) Title: LOW MOLECULAR WEIGHT WATER SOLUBLE POLYMER COMPOSITION AND METHOD OF USE

(57) Abstract: Novel low molecular weight ampholytic water soluble polymers are disclosed containing quaternary ammonium monomers; (meth)acrylic acid or 2-(meth)acrylamido-2-methylpropane sulfonic acid; and optionally a C_1-C_{22} alkyl (meth)acrylate acrylamide or methacrylamide and the use thereof in hair, skin and nail conditioning; paper coating; and subterranean well drilling and well cementing operations.

"LOW MOLECULAR WEIGHT WATER SOLUBLE POLYMER COMPOSITION AND METHOD OF USE"

FIELD OF THE INVENTION

The present invention relates to novel water soluble ampholyte polymers, polymer compositions and methods for using such polymers in applications wherein polymer deposition and substantivity is important. In particular, the polymers and polymer compositions of the present invention are low molecular weight ampholyte polymers and are useful in the treatment of substrates or used in combination with substrates such as those that are composed primarily of keratin, cellulose, minerals, pigments, clays and cement.

BACKGROUND OF THE INVENTION

The interaction of polyelectrolyte with substrates that carry a charge is at the heart of many industrial processes. The basic science that explains dispersion stabilization can be applied to many end use applications, such as paper coating, conditioning hair and skin, and suspension stabilization, as well as fluid loss control in oil field cementing and drilling operations.

For example, the surface properties of keratin are of interest in cosmetic science, and there has been a long-standing desire to discover ingredients, which will beneficially affect the topical and bulk condition of keratinous substrates, such as hair. The term "keratin"

used herein refers to human or animal hair, skin and/or nails. For example, such ingredients must have adequate adherent properties, so that they are not only adsorbed initially, but are also retained on exposure to water. This property is referred to as "substantivity", i.e., the ability of a material to be adsorbed onto keratin, or in the case of hair to penetrate into the hair shaft itself, resisting removal by water rinse-off.

Hair is composed of keratin, a sulfur-containing fibrous protein. The isoelectric point of keratin, and more specifically of hair, is generally in the pH range of 3.2-4.0. Therefore, at the pH of a typical shampoo, hair carries a net negative charge. Consequently, cationic polymers have long been used as conditioners in shampoo formulations, or as a separate treatment, in order to improve the wet and dry combability of the hair. The substantivity of the cationic polymers for negatively charged hair along with film formation facilitates detangling during wet hair combing and a reduction in static flyaway during dry hair combing. Cationic polymers generally also impart softness and suppleness to hair.

When cationic polymers are added to shampoos (or to skin care products such as cleaning compositions) containing anionic surfactants, formation of highly surface active association complexes generally takes place, which imparts improved foam stability to the shampoo. Maximum surface activity and foam stability, or lather, are achieved at near stoichiometric ratios of

anionic surfactant: cationic polymer, where the complex is least water soluble. Generally, cationic conditioners exhibit some incompatibility at these ratios. Compatibility gives a commercially more desirable clear formulation, while incompatibility leads to a haze or precipitation, which is aesthetically less desirable in some formulations.

In many situations, there is a trade off between high cationic charge content, which leads to good substantivity and the ability to formulate clear stable formulations. The need for a highly substantive water-soluble polymer that can be formulated into clear products is needed in the personal care industry.

In certain hair treatment applications, such as permanent waving, bleaching, and coloring hair, the use of common cationic conditioning polymers prior to treatment can lead to less than optimum performance. For example coloring can be uneven or the permanent wave and/or bleaching will damage hair. There remains a need in the hair treatment industry for an additive that will protect and/or condition the hair with no adverse consequences.

Polyelectrolytes are also used in the paper-coating end of the papermaking process. Papermaking, as it is conventionally known, is a process of introducing an aqueous slurry of pulp or wood cellulosic fibers (which have been beaten or refined to achieve a level of fiber hydration and to which a variety of functional additives

can be added) onto a screen or similar device in such a manner that the water is removed, thereby forming a sheet of the consolidated fibers, which upon pressing and drying can be processed into dry roll or sheet form.

Paper, used for instance in offset printing, usually requires the additional step of applying a pigmented coating to the surface of the paper. A typical coating compositions for offset printing comprises 100 parts by weight of pigment, from 5 to 25, and preferably from 10 to 20, parts by weight of an adhesive, a water soluble polymer dispersing agent for the pigment, auxiliary agents and water to give a total solids concentration of about 60% by weight. The adhesive is usually chosen from one or more of a protein derivative, a starch derivative, a cellulose derivative or a latex, and an example of a particular adhesive system would be 10 parts by weight of oxidized starch and 7 parts by weight of styrene-butadiene latex. The pigment would normally have a particle size distribution such that at least 80% by weight, and preferably at least 90% by weight, of its particles have an equivalent spherical diameter smaller than 2 micron in order to provide a coating of good gloss and brightness. The weight mean equivalent spherical diameter range for typical pigments suitable for offset coating compositions is from about 0.3 to about 0.8 micron. The water-soluble polymer dispersing agent for the pigment will typically be present at 0.1 to 2% of the paper coating composition and is required to prevent pigment settling prior to applying the coating to the paper surface. Many times the pigment is not adequately

dispersed, resulting in a lower gloss and lower brightness for the coated sheet.

A coating composition intended for use in preparing a coated paper for offset printing generally comprises a hydrophilic polymer material, such as a starch derivative or a cellulose derivative, in order to increase the initial viscosity of the composition and thus inhibit the penetration of the aqueous phase of the composition into the paper web. In the absence of a viscosifying hydrophilic polymer material, as soon as the coating composition contacts the paper web, the aqueous phase tends to be absorbed into the body of the paper, with the result that the local concentration of solids in the composition is increased and the composition becomes so viscous that the shear forces to which it is exposed in the paper coating apparatus render it virtually incapable of passing through the narrow clearance which exists between the applicator device and the moving web. When the hydrophilic polymeric material is present, the surface of the paper web is effectively sealed, thus inhibiting further penetration of the aqueous phase into the paper.

The term "paper, as used herein, includes sheet-like masses and molded products made from natural sources, synthetics such as polyamides, polyesters, rayon and polyacrylic resins as well as from mineral fibers such as asbestos and glass. In addition, paper made from combinations of cellulosic and synthetic materials are applicable herein. Paperboard is also included within the

broad term "paper".

There remains a need for a pigment dispersing agent that will maintain the pigment particles in suspension in the paper coating while improving the gloss and brightness of the final coated sheet.

In an ink jet recording method, recording is generally carried out by jetting fine drops of ink using a variety of mechanisms so as to form images on a recording paper. Therefore, the recording method of ink jet type has advantages in that it is less noisy, can provide full-color prints with ease and enables high-speed printing, compared with the recording method of dot impact type.

For the paper used in such an ink jet recording method, it is usually required to have properties of (1) ensuring high-speed drying of ink, (2) being free from cissing, feathering and overflowing of ink, (3) providing recorded images of high optical density, and (4) causing no rippling trouble upon absorption of ink.

In addition, ink jet printers have had remarkable development in recent years, so that they have come to ensure considerable colorfulness and vividness in the recorded images. Thus, recording media also have been required to be higher grade merchandise. As matters now stand, it is known that higher grade recorded image which can give such a feeling of higher quality as those provided by photography or high grade printed matter can

be obtained by choosing a recording medium having a glossy surface.

However, the need for reduction in running cost has also grown in proportion as prices of ink jet printers have declined. Since most of glossy recording media on the market use as their substrates more expensive materials, such as plastic films or laminated papers, they cannot meet the aforesaid need.

In contrast to the recording media on the market in which films or the like are used as substrate, cast-coated paper uses low-priced paper as a substrate and can be prepared in a relatively simple process, so that it has the advantage of a substantially lower cost. Further, as the recording side of cast-coated paper can be rendered glossy, the cast-coated paper is suitable for ink jet recording paper which can give a feeling of high quality and can provide high grade recorded images at a lower price.

High grade ink jet images depend on the formation of "dots" that contrast sharply with the color of the paper. If the ink jet dyes "wick" into the paper with the ink vehicle, "fuzzy" dot boundaries result and color intensity is decreased. There remains a need for a material that will substantively bind dye or pigment particles to the surface of ink jet printed paper so that sharply contrasting intense dots are formed.

Another area in which polyelectrolytes provide

benefit is in drilling fluids. It is well known that in perforating earthen formations to tap subterranean deposits such as gas or oil, that perforation is accomplished by well drilling tools and a drilling fluid. These rotary drilling systems consist of a drilling bit fitted with appropriate `teeth`, then a set of pipes assembled rigidly together end to end, the diameter of which is smaller than that of the drilling bit. This whole rigid piece of equipment, drill bit and drill pipe string, is driven into rotation from a platform situated above the well being drilled. As the drill bit attacks and goes through the geological strata, the crushed mineral materials must be cleared away from the bottom of the hole to enable the drilling operation to continue. Aqueous clay dispersion drilling fluids are recirculated down through the hollow pipe, across the face of the drill bit, and upward through the hole. The drilling fluid serves to cool and lubricate the drill bit, to raise the drilling cuttings to the surface of the ground, and to seal the sides of the well to prevent loss of water and drilling fluids into the formation through which the drill hole is being bored. After each passage through the well, the mud is passed through a settling tank or trough wherein the sand and drill cuttings are separated, with or without screening. The fluid is then again pumped into the drill pipe by a mud pump.

Some of the most serious problems encountered in producing and maintaining effective clay-based aqueous drilling fluids are caused by the interaction of the mud with the earth formation being drilled. These

interactions include contamination of the mud by formation fluids, incorporation into the mud of viscosity producing and inert drilled solids, chemical contamination by drilled solids, or by the infiltration of sea-water and/or fresh water. The conditions of high temperature and pressure inherent with deeper and deeper drilling operations, together with formation interactions, make drilling fluid behavior unreliable and difficult to reproduce.

Characteristics of an ideal drilling fluid would then include the following:

i) To have rheological characteristics as desirable as possible to be able to transport the mineral cuttings set in dispersion.

ii) To allow the separation of cuttings by all known means as soon as the mud flows out of the hole.

iii) To have such required density as to exert sufficient pressure on the drilled geological formations.

iv) To retain its fundamental rheological qualities as it is submitted, in very deep drilling, to higher and higher temperatures.

There remains a need for a material, which will provide these functions while not being degraded by the mechanical action of drilling.

Polyelectrolytes are also used in oil field cementing operations. Hydraulic cement compositions are used for carrying out various operations in oil, gas and water wells including, but not limited to construction and completion operations such as primary cementing and remedial operations such as squeeze cementing. Primary cementing involves the placement of a hydraulic cement composition into the annular space between the walls of a well bore and the exterior of a pipe such as casing disposed therein. The cement composition is pumped into the annular space and allowed to set into an annular cement sheath therein whereby the pipe is bonded to the walls of the well bore by the set cement.

As used herein, the term "cement" refers to portland cement, concrete and other mixtures of calcium oxide and sand.

Squeeze cementing techniques usually involve the undesirable movement of oil, gas or water through small holes or cracks in pipe disposed in the well bore; holes, cracks, voids or channels in the annular cement sheath between the pipe and the well bore; annular spaces between the cement sheath and the pipe or the walls of the well bore and permeable zones or fractures in subterranean formations. Such holes, cracks, etc. are plugged by squeezing hydraulic cement compositions therein which harden and form impermeable plugs.

In performing cementing operations in such wells, the cement compositions are often subjected to high

temperatures, particularly when the cementing is carried out in deep subterranean zones. The high temperatures can cause premature setting of the cement compositions, i.e., the compositions can not be pumped for long enough times before setting to place them in the zones to be cemented. This requires the use of set retarding additives in the cement compositions which extend the setting times of the compositions so that adequate pumping time is provided in which to place or displace the compositions into desired subterranean zones.

There remains a need for a polymer, which will not degrade under the temperatures, pressures and mechanical action of oil field cementing operations.

In all of the applications outlined above, polymers have been used to improve the properties of the substrate or minimize adverse consequences. For example if the substrate is hair, polymers have been used to improve the detangling and combing of hair after shampooing. During paper coating, polymers are used to provide stable pigmented compositions that add brightness and gloss to the coated sheet. Polymers are also added to paper coatings to provide a surface that results in fast drying well defined dots from the ink jet printing process. Polymers are added to drilling fluids and cementing compositions to aid in performance and minimize water loss to the surrounding rock formation. In all of these applications, the polymer must be substantive to the substrate, meaning that it will adhere or adsorb onto the substrate surface and/or penetrate into the substrate

structure such that it will not be easily removed. Although many polymers are used in the aforementioned applications, there still remains a shortcoming in that they can be removed from the substrate due to physical action.

U.S. Patent No. 4,842,849 discloses compositions suitable for treating keratin comprising at least one cationic polymer including poly(dimethyldiallylammonium chloride), and at least one anionic polymer containing vinylsulfonic groups, optionally copolymerized with acrylamide. The cationic polymer may be an amphoteric polymer as defined.

EP 0 080 976 discloses aqueous hair-cosmetic compositions containing a surface active polymeric acrylic-based quaternary ammonium salt, a monomeric or oligomeric ammonium salt, and a surface active nonionic, anionic or zwitterionic component.

U.S.Patent Nos. 4,128,631 and 4,065,422 disclose a method of imparting lubricity to keratinous substrates such as skin or hair by contacting said substrates with a salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPSA) having a molecular weight of from 1-5 million.

U.S. Patent No. 4,772,462 discloses hair products containing a copolymer of dimethyl diallyl ammonium chloride and acrylic acid. These polymers are limited in that they rely solely on ionic interactions to be substantive to substrates.

U.S. Patent Nos. 5,296,218; 5,609,862; and 5,879,670 disclose ampholyte polymers including polymers providing superior conditioning properties in shampoos and other hair care products. These polymers also rely primarily on ionic interactions for substantivity, however, the ionic charge is pH dependent which limits utility.

U.S. Patent Nos. 4,455,240; 4,652,623; 4,726,906; and 5,032,295 disclose ampholyte polymers for use as filtration control aids in drilling muds. These polymers rely only on ionic interactions to achieve substantivity, however, the charge in the polymers changes with pH which limits utility.

SUMMARY OF THE INVENTION

The composition comprises a low molecular weight water soluble ampholyte polymer containing monomer moieties of: (a) 1 to 98 mol % of a monomer selected from the group consisting of acrylamidopropyltrimethyl ammonium halide, methacrylamidopropyltrimethyl ammonium halide, methyloyloxyethyl trimethyl ammonium halide, methyloyloxyethel trimethyl ammonium methylsulfates, acryloyloxyethyl trimethylammonium halide, and dimethyl diallyl ammonium halide; b) 1 to 90 mol % of a monomer selected from the group consisting of acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid and 2-methacrylamido-2-methylpropane sulfonic acid; and (c) 0 to about 80 mol % of a nonionic monomer selected from the group consisting of C_1-C_{22} alkyl

acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkylacrylamide, methacrylamide, n-alkylmethacrylamide, and diacetone acrylamide; wherein the weight average molecular weight of said polymer, as determined by viscometry, is less than about 10,000.

DETAILED DESCRIPTION OF THE INVENTION

The water soluble ampholyte polymers of the present invention and compositions containing such polymers are novel and unexpected because of their unique structure, molecular weight, and improved substantivity. Specifically, it has been found that high molecular weight polymers (polymers with molecular weight greater than 10,000) interfere with certain end use applications. For example, some high molecular weight polymers, such as those greater than 100,000, can cause uneven hair coloring, poor holding permanent waves, or less than optimal conditioning. Other high molecular weight polymers will cause a build up of viscosity in dispersions when low viscosity dispersions are required. The water-soluble polymers of the present invention overcome these difficulties as outlined below.

The instant invention is directed to novel low molecular weight water soluble ampholyte polymers and polymer compositions and to the use of the same in the treatment of various substrates such as keratin, cellulose, paper, pigments, minerals, clays or cements.

As used herein, keratin substrates include, but are not limited to, animal and human hair, skin and nails.

Cellulosic substrates include, but are not limited to paper, cardboard and films. Minerals include, but are not limited to calcium carbonate, aluminum oxide, calcium sulfate and talc. Pigments include, but are not limited to titanium dioxide and iron oxide. Clays include, but are not limited to kaolinite, bentonite and anorthite. Cement includes, but is not limited to portland cement, concrete and other mixtures of calcium oxide and sand.

A particular embodiment of the instant invention is directed to a low molecular weight linear ampholyte polymer prepared from or comprising monomer moieties of: (a) 1 to about 98 mol %, of at least one monomer selected from the group consisting of acrylamidopropyl-trimethyl ammonium chloride (APTAC), methacrylamidopropyltrimethyl ammonium chloride (MAPTAC), methyloyloxyethyl trimethyl ammonium chloride (METAC) methyloyloxyethyl trimethyl ammonium methylsulfate (METAMS), acryloyloxyethyl trimethyl ammonium chloride (AETAC) and/or dimethyl diallyl ammonium chloride (DMDAAC); (b) 1 to about 80 mol % of a monomer selected from the group consisting of acrylic acid (AA), methacrylic acid (MAA), 2-acrylamido-2-methylpropane sulfonic acid (AMPSA) and/or 2-methacrylamido-2-methylpropane sulfonic acid (MAMPSA); and (c) 0 to about 70 mol percent, of a nonionic monomer selected from the group consisting of C_1-C_{22} alkyl acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkylmethacrylamide and/or diacetone acrylamide. Preferably, the mol ratio of a) : b) in said linear ampholytic polymer ranges from about 20:80 to about 95:5, more preferably from about 25:75 to

about 75:25.

Further, the weight average molecular weight of said polymer, as determined by viscometry, is less than about 10,000, preferably less than about 5,000, more preferably less than about 2,000. Alternatively, gel permeation chromatography (GPC) with light scattering detection can be used. There is a practical lower limit of the low molecular weight polymer of about 300. The molecular weight is preferably at least 1,000.

Preferably, the mol ratio of a):b) ranges from 25:75 to about 75:25, and the preferred polymers contain c), the nonionic monomers in an amount of at least about 1 up to about 50 mol % of the above-defined C_1-C_{22} acrylate or C_1-C_{22} methacrylate esters, acrylamides or methacrylamides. More preferably, the instant polymers contain about 5 to about 35 mol % of the C_1-C_{22} alkyl acrylate or C_1-C_{22} alkyl methacrylate esters, acrylamides or methacrylamides. In the most preferred case, the nonionic monomer (c) is methyl acrylate, methyl methacrylate, acrylamide or methacrylamide.

The instant invention in this embodiment is also directed to a low molecular weight water soluble linear ampholyte polymer comprising:

a) about 20 to about 95 mol % APTAC, MAPTAC, METAC, METAMS, AETAC or DMDAAC, preferably MAPTAC or DMDAAC;
b) about 5 to about 70 mol % acrylic acid, methacrylic acid, AMPSA or MAMPSA, preferably acrylic acid; and

c) 0.1 to about 60 mol %, preferably 1 to about 50 mol %, of a C_1-C_{22} alkyl acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkylmethacrylamide and/or diacetone acrylamide, preferably methyl acrylate, methyl methacrylate, acrylamide and methacrylamide and most methyl acrylate and acrylamide, wherein the molecular weight of said polymers is less than about 10,000.

Most preferably, the instant invention in this embodiment is directed to a water soluble linear ampholyte polymer comprising:

a) about 25 to about 75 mol % DMDAAC, APTAC or MAPTAC;

b) about 25 to 60 mol % acrylic acid or methacrylic acid; and

c) about 1 to about 35 mol % of a C_1-C_3 alkyl acrylate, C_1-C_3 alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkylmethacrylamide and/or diacetone, wherein the molecular weight of said polymer is less than about 10,000.

In an alternative embodiment of the present invention, the polymer can be prepared by conventional polymerization techniques followed by physical separation of the low molecular weight polymer from a polymer composition, which contains high molecular weight polymer as part of its molecular weight distribution. Techniques for this type of separation are well known to those skilled in the art of water-soluble polymer processing and are typically referred to as molecular weight fractionation techniques. Although it is not the

intention to be limited to a single method, fractionation techniques include the use of non-solvents (alcohols or hydrocarbons in which the high molecular weight polymer are not soluble) to precipitate the high molecular weight polymer, leaving in solution the low molecular weight polymer of the present invention. Alternatively, appropriate non-solvents and pH can be use to cause two liquid phases to form. One containing high molecular weight polymer and the other containing the low molecular weight polymer of the present invention. Another embodiment would include the use of ultrafiltration or nanofiltration devices can be used to physically separate the low molecular weight polymer of the present invention from a polymer composition, which contains the undesired high molecular weight polymer. Still another method would involve drying the polymer and extracting the desired low molecular weight polymer through the use of appropriate solvents. Examples of appropriate non-solvents, phase separating and extraction solvents would include ethanol, methanol, isopropanol and other lower alkyl alcohols, acetone, methyl ethyl ketone and other lower alkyl ketones and super critical carbon dioxide (carbon dioxide at temperatures and pressures where it is in liquid form).

Further, the instant invention is directed to a method for treating a substrate comprising contacting said substrate with the above defined fractionated polymer, preferably with an effective amount of said polymer or, an effective amount of an acceptable medium comprising from about 0.01 to about 20%, preferably from

about 0.1 to about 10%, by weight, based on the total weight of said medium, of an instant fractionated polymer.

As used herein, the term "active basis" refers to a concentration of additive based on the active solids in the stock solution.

As used herein, the term "effective amount" refers to that amount of a composition necessary to bring about a desired result, such as, for example, the amount needed to treat a keratin-containing substrate relative to a particular purpose, such as conditioning or the amount of a composition necessary to provide good ink jet printing on paper, such as minimal feathering.

Turning now to each of the components of the instant ampholyte polymers, the cationic component is either acrylamidopropyl-trimethyl ammonium chloride (APTAC), methacrylamidopropyl-trimethyl ammonium chloride (MAPTAC), dimethyl diallyl ammonium chloride (DMDAAC), methacryloyloxy ethyl-trimethyl ammonium chloride (METAC), methacryloyloxy ethyl-trimethyl ammonium methyl sulfate (METAMS), or acryloyloxy ethyl-trimethyl ammonium chloride (AETAC) which may be represented as follows:

MAPTAC

$CH_2 = C(CH_3) - CO - NH - CH_2 - CH_2 - CH_2 - N^+ - (CH_3)_3$

- counter ion, preferably a halogen such as Cl^-.

APTAC

$CH_2 = CH - CO - NH - CH_2 - CH_2 - CH_2 - N^+ - (CH_3)_3$
- counter ion, preferably a halogen such as Cl^-

METAC/METAMS

$CH_2 = C(CH_3) - CO - O - CH_2 - CH_2 - N^+(CH_3)$
- counter ion, preferably methylsulfate (METAMS), chloride (METAC) or other halogen

AETAC

$CH_2 = CH - CO - O - CH_2 - CH_2 - N^+(CH_3)_3$
- counter ion chloride or other halogen

DMDAAC

$CH_2 = CH - CH_2 - N^+(CH_3)_2 - CH_2 - CH = CH_2$
- counter ion chloride or other halogen

The cationic monomer portion of the ampholyte polymers of the instant invention is present in an amount such that the cationic:anionic mol ratio ranges from about 20:80 to about 95:5

The second component of the ampholyte polymers of the present invention is the anionic monomer acrylic acid (AA) or methacrylic acid (MAA), which may be represented by the following formula:

$$CH_2 = C(R) - COOH$$

where R is H or CH_3.

Additionally, 2-acrylamido-2-methylpropane sulfonic

acid (AMPSA) or 2-methacrylamido-2-methylpropane sulfonic acid (MAMPSA), preferably AMPSA, can be used as component (b), alone or in combination with acrylic acid or methacrylic acid. These monomers are represented as follows:

$$CH_2 = C(R) - CO - NH - C(CH_3)_2 - CH_2 - SO_3^{-}X^{+}$$

wherein R = H or CH_3 and X = suitable salt forming cation.

The third mer unit of the instant invention is an alkyl acrylate, methacrylate represented as follows:

$$CH_2 = C(R^1) - CO - O - R^2$$

wherein R^1 = H or CH_3 and R^2 = C_1-C_{22} linear or branched alkyl

Acrylamide

$CH_2 = CH - CO - NH_2$

Methacrylamide

$CH_2 = C(CH_3) - CO - NH_2$

n-Alkyl acrylamide

$CH_2 = CH - CO - NHR$

$R = C_1 - C_{22}$ linear or branched alkyl

n-AlkylMethacrylamide

$CH_2 = C(CH_3) - CO - NHR$

$R = C_1 - C_{22}$ linear or branched alkyl

Diacetone Acrylamide

$CH_2 = CH - CO - NH - C(CH_3)_2 - CH_2 - CO - CH_3$

The instant polymers may be prepared by conventional solution polymerization techniques, as indicated below and in the Examples. Thus, to prepare the instant polymers the appropriate weights for the desired mol %'s of DMDAAC/APTAC/MAPTAC, acrylic are charged to a glass beaker equipped with a stirring means. The desired amount of alkyl acrylate, methacrylate or acrylamide is then added to the beaker with vigorous stirring to give the desired total monomer concentration, which is generally about 10-50% by weight. The monomer mixture may then be adjusted to a pH of about 3.0 to about 6.5 with dilute NaOH. Water is added to a resin kettle, which is equipped with a condenser, heating mantle and mixer and heated to about 85°C. The polymerization is then conducted by co-feeding the monomer mixture, a sodium persulfate solution and a sodium bisulfite solution over a 90 minute period. After the feed period is completed, additional dilution water and sodium bisulfite are added to scavenge any residual monomer and to dilute the final product to 10 - 40% polymer solids.

The molecular weight of the ampholyte polymers of the present invention may be within the broad range of less than about 10,000, preferably less than about 5,000, and more preferably less than about 2,000.

Reduced viscosity (dl/g) may be used as an approximate measure of the weight average molecular

weight of the ampholyte polymers of the present invention. The values shown herein represent a capillary viscosity measured with Ubbelhhde Capillary Viscometer at 40% concentration of polymer in a 1M NaCl solution, pH 7, at 30° C. The resulting molecular weight value is calculated in accordance with methods well known in the art.

Cosmetically Acceptable Media

The water soluble polymers of the present invention are used as compositions for treating hair, skin and nails by incorporating them in a cosmetically acceptable medium in amounts from about 0.1 to about 20% by weight of said polymer, preferably in an amount from about 0.5 to about 10% by weight of said water soluble polymer, with an amount of about 1 to about 5% being most preferred.

These compositions can be presented in various forms, i.e., various cosmetically acceptable media, such as a liquid, cream, emulsion, gel, thickening lotion or powder; they can contain water and also any cosmetically acceptable solvent, in particular monoalcohols, such as alkanols having 1 to 8 carbon atoms, like ethanol, isopropanol, benzyl alcohol and phenylethyl alcohol, polyalcohols, such as alkylene glycols, like glycerins, ethylene glycol and propylene glycol, and glycol ethers, such as mono-, di- and tri-ethylene glycol monoalkyl ethers, for example ethylene glycol monomethyl ether,

ethylene glycol monomethyl ether and diethylene glycol monomethyl ether, used singly or in a mixture. These solvents can be present in proportions of up to as much as 70% by weight, relative to the weight of the total composition.

These compositions can also be packaged as an aerosol, in which case they can be applied either in the form of an aerosol spray or in the form of an aerosol foam.

As the propellant gas for these aerosols, it is possible to use, in particular, dimethyl ether, carbon dioxide, nitrogen, nitrous oxide and volatile hydrocarbons, such as butane, isobutane, propane and, possibly, chlorinated and fluorinated hydrocarbons, although the latter are falling into increasing environmental disfavor.

Preferred compositions can also contain electrolytes, such as aluminum chlorhydrate, alkali metal salts, e.g., sodium, potassium or lithium salts, these salts preferably being halides, such as the chloride or bromide, and the sulphate, or salts with organic acids, such as the acetates or lactates, and also alkaline earth metal salts, preferably the carbonates, silicates, nitrates, acetates, gluconates, pantothenates and lactates of calcium, magnesium and strontium.

These compositions can also be presented in the form of a powder or of lyophilisates to be diluted before use.

The compositions according to the present invention can contain any other ingredient normally used in cosmetics, such as perfumes, dyestuffs which can serve to color the composition itself or the fibres of the hair, preservatives, sequestering agents, thickeners, silicones, softeners, foam synergistic agents, foam stabilisers, sun filters, peptising agents and also anionic, non-ionic,cationic or amphoteric surface-active agents or mixtures thereof.

These compositions can be used, in particular, in the form of a shampoo, a rinsing lotion, a cream or a treatment product which can be applied before or after coloring or bleaching, before or after shampooing, before or after perming or before or after straightening, and can also adopt the form of a coloring product, a setting lotion, a brushing lotion, a bleaching product, a perming product or a straightening product.

A particularly preferred embodiment consists of use in the form of a shampoo for washing the hair.

In this case, these compositions contain anionic, cationic, nonionic or amphoteric surface-active agents typically in an amount from 3 to 50% by weight, preferably 3 to 20%, and their pH is 3 to 10, preferably 4 to 9 and most preferably 4.5 to 8.5.

A list of the surface-active agents, which can be used according to the invention, is given in U.S. Pat.

Nos. 4,240,450; 4,445,521; and 4,719,099.

Another preferred embodiment consists of use in the form of a rinsing lotion to be applied mainly before or after shampooings. These lotions are typically aqueous or aqueous-alcoholic solutions, emulsions, thickened lotions or gels. If the compositions are presented in the form of an emulsion, they can be nonionic, anionic or cationic. The nonionic emulsions consist mainly of a mixture of an oil and/or a fatty alcohol with a polyoxyethyleneated alcohol, such as polyoxyethyleneated stearyl or cetyl/stearyl alcohol, and cationic surface-active agents can be added to these compositions. The anionic emulsions are formed essentially from soap.

If the compositions are presented in the form of a thickened lotion or a gel, they contain thickeners in the presence or absence of a solvent. The thickeners which can be used are especially carbopol, xanthan gums, sodium alginates, gum arabic and cellulose derivatives, and it is also possible to achieve thickening by means of a mixture of polyethylene glycol stearate or distearate or by means of a mixture of a phosphoric acid ester and an amide. The concentration of thickener is suitably 0.05 to 15% by weight. If the compositions are presented in the form of a styling lotion, shaping lotion or setting lotion, they generally comprise, in aqueous, alcoholic or aqueous-alcoholic solution, the low molecular weight ampholyte polymers defined above.

The compositions of the invention are also intended

for use in the dyeing or bleaching of keratin fibres, and in particular human hair, they contain at least one oxidation dyestuff precursor and/or one direct dyestuff, in addition to the ampholyte polymer. They can also contain any other adjuvant normally used in this type of composition. In many instances when this polymer is used, the hair dye is more resistant to removal by shampooing.

The pH of the dyeing or bleaching compositions is generally 7 to 11, and can be adjusted to the desired value by adding an alkalizing agent.

The composition according to the present invention can also be used for waving or straightening the hair. In this case, the composition contains, in addition to the ampholyte polymer, one or more reducing agents and, if appropriate, other adjuvants normally used in this type of composition; such compositions are intended for use conjointly with a neutralizing composition.

The composition according to the present invention can also be used for skin care products such as those that are primarily "leave on" formulations such as lotions, emulsions, creams, and sunscreen formulations. Other skin care products would include "rinse off" formulations such as bar soaps, liquid hand soaps, disinfecting soaps and shower gels. These "rinse off" formulations can be comprised of a variety of surfactants as outlined above, alkali salts of fatty acids (soaps) or combinations of each.

The composition of the instant invention can generally be successfully added to aqueous paper coating formulations. The paper coating formulation will comprise 0.1 to 5 weight % of the polymer of the present invention, 10 to 70 % by weight of pigment, from 5 to 25 % by weight of an adhesive, auxiliary agents and water to give a total solids concentration of about 40 to 80% by weight. The resulting paper will have improved gloss, brightness, and improved ink jet printing quality.

The instant invention is also directed to a method for drilling a well in a subterranean formation comprising circulating into the well, during drilling an aqueous drilling fluid, the improvement wherein said aqueous drilling fluid comprises:

(a) an aqueous clay dispersion; and

(b) the above-described polymer.

The clay dispersion may be any finely divided solid which is capable of being dispersed or suspended in an aqueous liquid vehicle. Ordinarily, such material will include hydratable clay or colloidal clay bodies such as Wyoming bentonite, commercial medium-yield drilling clays mined in various parts of the country such as in Texas, Tennessee and Louisiana, and those produced when clay subsurface formations are drilled. Weighting materials added to increase specific gravity such as barites, iron oxide, and the like may also be included.

The aqueous medium may be fresh water such as is obtained from wells or streams; it may be salt water from the sea or from wells; or, it may even include oil-in-water emulsions, i.e., water which has become contaminated in some way with small quantities of oil, or to which such oil has been added to gain some desired advantage. The polymers of the instant invention were found to be particularly effective in salt water and to be stable at high temperature. The drilling mud containing the polymers of the instant invention show both good filtration and rheology properties.

It is contemplated that the drilling muds of the invention may also contain other additives besides the polymers of the invention. Materials such as caustic, quebracho, lime and the like may be added to the drilling mud at the surface while other materials such as gypsum, shale and the like may be encountered in subsurface formations during drilling operations.

When employed in accordance with the invention, the polymer may be added directly to the drilling mud as a dry powder, as a slurry suspended in a suitable liquid, or as a solution in water or some other suitable solvent, and they may be incorporated therein at any convenient point in the mud circulation system. It may be desirable to employ a mixing device such as a cone and jet mixer or the equivalent for incorporating the additive in the mud.

The present invention is also directed to cementing

compositions that are useful in oil, gas and water well cementing operations since such compositions have reduced fluid loss to the surrounding formation. Such compositions are used to cement a conduit penetrating a permeable earthen formation via introducing such composition into the space between such conduit and such formation and allowing the composition to harden. These cementing compositions for use in oil, gas and water well cementing operations comprise water, hydraulic cement, and the ampholyte polymer of the present invention.

EXAMPLES

Example 1 - PREPARATION OF a 45/45/10 M/M AQUEOUS SOLUTION POLYMER OF AA/MAPTAC/Methyl Acrylate

A 45/45/10 M/M/M polymer of acrylic acid, MAPTAC and methyl acrylate was prepared as follows:

1. Zeolite softened water (item 1 in Table 1, below) was added to a resin kettle equipped with stirrer, condenser, thermometer and heating mantle. The water was heated to 85 °C and purged with nitrogen for 30 minutes.

2. Acrylic Acid, 50% aqueous MAPTAC solution, and methyl acrylate (Items 2, 3, and 4 in Table 1, below) were added to a glass beaker in the amounts shown, and stirred until uniform.

3. Sodium Persulfate and Zeolite softened water (items 5 and 1 in Table 1, below) were added to a separate glass beaker in the amounts shown, and stirred until uniform.

4. Sodium bisulfite solution (item 6 in Table 1, below) was added to a separate glass beaker in the amounts shown.

5. Beginning at the same time, the mixture from (2) was fed to the resin kettle uniformly over a 90 minute period and the mixtures from (3) and (4) were fed to the resin kettle uniformly over a 90 minute period. The nitrogen purge was maintained throughout the feed period.

6. After the feeds were complete, the solution was held at 85 °C with a nitrogen blanket for 30 minutes.

7. 35% aqueous hydrogen peroxide (item 7 in Table 1, below) was added and left to react for 15 minutes.

8. 50% aqueous Sodium hydroxide and Zeolite softened water (items 8 and 1 in Table 1, below) were added to the resin kettle and the contents cooled to room temperature.

The resulting polymer solution, which represents the best mode known to the inventors, had a reduced viscosity measured at 4.0% in 1N NaCl at 30 °C of 0.04 dl/g.

TABLE 1

AA/MAPTAC/methyl Acrylate polymer 45/45/10 m/m/m

ITEM	NAME	WEIGHT %
1	Zeolite Softened Water	24.81
2	MAPTAC, 20% active	42.67
3	Methyl Acrylate, 99% active	1.70
4	Acrylic Acid, 100% active	6.96
5	Sodium Persulfate, 100% active	0.61
6	Sodium Bisulfite, 38% active	21.44
7	Hydrogen Peroxide, 35% active	0.08
8	Sodium Hydroxide 50% active	1.73

Example 2

Two lotions (one with and one without the polymer of example 1 as in Table 2, below) and a developer (Table 3, below) are prepared by mixing the separate components. When the lotions are mixed with the developer solution, a gelled hair coloring composition is prepared which colors human hair when applied thereto and thoroughly incorporated in the hair by finger manipulation.

TABLE 2

DYE LOTION

	Weight % in formula	
	Formula 1	Formula 2
p-Phenylenediamine	0.020	0.020
Resorcinol	0.030	0.030
1-Naphthol	0.010	0.010
Sodium Sulfite	0.100	0.100
Erythorbic Acid	0.200	0.200
EDTA	0.020	0.020
Polymer of example 1	4.000	0.000
Hexylene Glycol	3.500	3.500
Sodium Laureth Sulfate	1.000	1.000
28% Ammonia	7.000	7.000
Water	84.120	88.120

TABLE 3

DEVELOPER

	Wieght % in formula
Hydrogen Peroxide	3.000
Aculyn-33[1]	6.700
Disodium EDTA	0.100
Nonoxynol-9	0.400
Nonoxynol-4	0.200
Water	89.600

[1]anionic polymer available from Rohm and Haas Company

After twenty minutes the dye/developer are rinsed from the hair with water and the hair is allowed to air dry overnight at 70 °C, 50% relative humidity. The hair

treated with dye lotion 1 is colored better than the hair treated with dye lotion 2 (increased dye deposition and/or more uniform dye coverage).

Example 3

An aqueous clay based drilling mud is prepared using the polymer of Example 1 (45/245104 m/m/m AA/MAPTAC/Methyl Acrylate) as outlined in Table 4.

Table 4

Clay Based Gypsum Drilling Mud

Ingredient	Percent (w/w %)
Water	86.0
Bentonite	3.5
Rev Dust	7.5
Gypsum	1.0
Lignonsulfate	1.0
Polymer of Example 1	0.5
Caustic	0.5

The clay based gypsum drilling mud is aged for 16 hours at 325 °F and then cooled. The resulting API filtrate reading is lower for the formula of the example when compared to a corresponding clay based gypsum drilling mud without polymer.

Example 4

A cementing composition is prepared using the polymer of Example 1 (45/45/10 m/m/m AA/MAPTAC/Methyl

Acrylate) as outlined in Table 5.

Table 5

Cementing Composition

Ingredient	Percent (w/w %)
Water	46.0
Class H Cement	43.0
Polymer of Example 1	1.0

The cementing composition is mixed into a slurry. The resulting API filtrate reading (30 minute, 125 °F, 1,000 psi) is lower for the formula of the example when compared to a corresponding cementing composition without polymer.

WHAT IS CLAIMED IS:

1. A low molecular weight water soluble ampholyte polymer composition containing monomer moieties comprising:
(a) 1 to 98 mol % of a monomer selected from the group consisting of acrylamidopropyltrimethyl ammonium halide, methacrylamidopropyltrimethyl ammonium halide, methyloyloxyethyl trimethyl ammonium halide, methyloyloxyethel trimethyl ammonium methylsulfates, acryloyloxyethyl trimethylammonium halide, and dimethyl diallyl ammonium halide; b) 1 to 90 mol % of a monomer selected from the group consisting of acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid and 2-methacrylamido-2-methylpropane sulfonic acid; and (c) 0 to about 80 mol % of a nonionic monomer selected from the group consisting of C_1-C_{22} alkyl acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkylacrylamide, methacrylamide, n-alkylmethacrylamide, and diacetone acrylamide; wherein the weight average molecular weight of said polymer, as determined by viscometry, is less than about 10,000.

2. The polymer composition according to Claim 1, wherein a) is methacrylamidopropyltrimethyl ammonium chloride (MAPTAC), b) is acrylic acid, and c) is methyl methacrylate.

3. The polymer composition according to Claim 1, wherein said molecular weight is less than about 5,000.

4. The polymer composition according to Claim 1, wherein the mol ratio of a) : b) ranges from 25:75 to about 75:25.

5. A low molecular weight water soluble ampholyte polymer composition containing monomer moieties comprising :

a) about 20 to about 95 mol.% APTAC, MAPTAC, MBTAC, MBTAMS, AETAC, or DMDAAC;

b) about 5 to about 70 mol % acrylic acid, methacrylic acid, AMPSA or MAMPSA; and

c) about 0.1 to about 60 mol % a C_1- C_{22} alkyl acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkyl methacrylamide, or diacetone acrylamide wherein the molecular weight of said polymer is less than about 10,000.

6. A low molecular weight water soluble ampholyte polymer containing monomer moieties comprising:

a) about 25 to about 75 mol % APTAC, MAPTAC, or DMDAAC;

b) about 25 to about 60 mol % acrylic acid, methacrylic acid; and

c) about 1 to about 35 mol % of a C_1-C_3 alkyl acrylate, C_1-C_3 alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkyl methacrylamide, or diacetone acrylamide wherein the molecular weight of said polymer is less than about 10,000.

7. A low molecular weight water soluble linear ampholyte polymer composition containing monomer moieties comprising :

a) about 20 to about 95 mol % APTAC, MAPTAC, MBTAC, MBTAMS, AETAC, or DMDAAC;

b) about 5 to about 70 mol % acrylic acid, methacrylic acid, AMPSA or MAMPSA; and

c) about 0.1 to about 60 mol % a C_1- C_{22} alkyl acrylate, C_1-C_{22} alkyl methacrylate, acrylamide, n-alkyl acrylamide, methacrylamide, n-alkyl methacrylamide, or diacetone acrylamide; wherein the molecular weight of the resulting polymer is less than 10,000.

8. A composition for treating hair, skin and nails which comprises 0.1 to 20% by weight of the composition of Claim 7 in a cosmetically acceptable medium.

9. A method for coating paper or paperboard wherein the linear ampholyte polymer of Claim 1 is added to a pigmented paper coating composition.

10. A method for drilling a well in a subterranean formation, comprising circulating into the well, during drilling, an aqueous drilling fluid comprising an aqueous clay dispersion and the low molecular weight water soluble ampholyte polymer composition of Claim 1.

11. A method of cementing a conduit in a borehole penetrating an earthen formation by introducing a cementing composition into the space between said conduit and said formation, wherein said cementing composition comprised water; cement; and from about 0.1% to about 1.5% by weight of cement of the low molecular weight water soluble ampholyte polymer composition of Claim 1.

12. A method for treating hair, skin or nails wherein the low molecular weight water soluble ampholyte polymer of Claim 1 is added to a cosmetically acceptable medium.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15343

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :A61K 7/06; C08F 30/02, 228/02; C09K 7/02
US CL : 424/70.16, 70.17, 78.03; 526/273, 277, 278, 287, 288; 252/8.51
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/70.16, 70.17, 78.03; 526/273, 277, 278, 287, 288; 252/8.51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

West 2.0

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,032,295A [MATZ et al] 16 July 1991, see col.2, lines 4, 36-65, col.3, lines1-3, 18-36, col.4, lines8-16, 28-42, 49-55, claims 1, 3, 7,9, 13, 14.	1,3-7,10,11
X	US 4,726,906 A[CHEN et al] 23 February 1988, see abstract, col.2, lines 56-68 claims 1-3.	1,3,7-10,11
Y	US 5,879,670 A [MELBY et al] 09 March 1999, see abstarct col. 4, lines 58-67, col.5, lines 1-20, col.6, lines 43-60.	1-9, 12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 AUGUST 2000	14 SEP 2000

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